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## PROVISIONAL APPLICATION FOR PATENT COVER SHEET

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## PERSONAL CARE FIXATIVE

### BACKGROUND OF THE INVENTION

Recent regulatory legislation and environmental concerns require that personal care fixatives contain lower levels of volatile organic compounds (VOC) than are  
5 presently found in many commercially available fixative products. For example, desirable hair fixative compositions should have VOC levels of less than about 55 weight percent and should exhibit little or no loss in curl retention in humidity conditions, good holding power, ease of removal and resistance to build up.

A need exists for a personal care fixative that contains lower levels of volatile  
10 organic compounds than the VOC levels found in currently available fixative products while retaining or improving upon the fixative properties of those currently available fixative products.

### SUMMARY OF THE INVENTION

The present invention is directed to bimodal polymer compositions and personal  
15 care fixatives containing bimodal polymer compositions. The present invention includes a bimodal polymer composition having a first polymer with anionic character and a second polymer with cationic character and wherein the polymers form an interpenetrating polymer network. In one embodiment, the present invention also includes personal care fixatives (*e.g.*, health care, hygiene or cosmetic compositions)  
20 containing the bimodal polymer composition.

The present invention also includes methods for forming a bimodal polymer composition. In one embodiment, a method for forming a bimodal polymer composition includes the step of polymerizing monomers to form a first polymer with cationic character in the presence of a second polymer with anionic character. In  
5 another embodiment, a method for forming a bimodal polymer composition includes the step of polymerizing monomers to form a first polymer with anionic character in the presence of a second polymer with cationic character.

A method for forming a bimodal polymer composition is also described herein that includes the step of polymerizing monomers to form a first polymer with cationic  
10 character in the presence of a second polymer with anionic character wherein the first polymer is formed from a monomer composition including about 35 to about 45 weight percent ammonium derivative monomer, about 15 to about 30 weight percent water insoluble monomer, and about 5 to about 15 weight percent water soluble monomer.

Personal care fixatives containing the present bimodal polymer compositions can  
15 contain lower levels of volatile organic compounds than the VOC levels found in currently available fixative products. In addition, the present personal care fixatives can have acceptable, or even improved, fixative properties.

Personal care fixatives containing bimodal polymer compositions of the present invention can gel at relatively low solids concentrations and/or at relatively high  
20 humidity conditions. Without being held to any particular theory, the ability of the present fixatives to gel at relatively low solids concentrations and/or at relatively high humidity conditions is thought to be due to ionic bonding of the bimodal polymer composition's polymer constituents. The present personal care fixatives can also gel quickly, allowing fixatives with dilute concentrations of the bimodal polymer  
25 composition to hold keratin-type substrates (*e.g.*, hair) while volatile substances contained therein, such as water or alcohol, evaporate. This quick gelling makes the bimodal polymer compositions of the present invention particularly valuable for producing personal care fixatives that contain low VOC concentrations. In addition, ionic cross-linking is thought to produce good adhesion to keratin-type substrates due to

an increase in cohesive energy density provided by polar groups contained in the bimodal polymer compositions.

The bimodal polymer compositions of the present invention have acceptable adhesion to keratin-type substances such as hair, skin, fingernails, and toenails. The  
5 bimodal compositions described herein can form polymer films with acceptable adhesion in relatively high humidity conditions from personal care fixatives having relatively low concentrations of volatile organic compounds. The polymer films formed from these inventive personal care fixatives can also provide improved film properties, for example, gloss, water resistance, and abrasion resistance, in a variety of personal  
10 care applications.

The bimodal polymer compositions of the present invention represent a significant advance over mere blends of polymers. Without being held to any particular theory, it is believed that blends of polymers containing anionic and cationic character can have only very limited stability. Further, it is believed that blends of polymers  
15 containing anionic and cationic character are limited in their ability to complex ionically. The bimodal polymer compositions of the present invention can have increased stability over polymer blends. In addition, it is believed that the present bimodal polymer compositions contain ionic moieties (*e.g.*, groups having anionic and cationic functionalities) in close proximity to each other, whereby the polymer chains  
20 can interact in a manner generally not possible in a blend of polymers.

#### DETAILED DESCRIPTION OF THE INVENTION

A description of preferred embodiments of the invention follows.

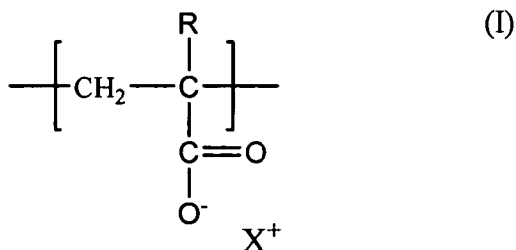
The present invention is directed to bimodal polymer compositions and personal care fixatives containing bimodal polymer compositions. The present invention  
25 includes a bimodal polymer composition having a first polymer with anionic character and a second polymer with cationic character and wherein the polymers form an interpenetrating polymer network.

“Bimodal,” as that term is used herein, describes polymer compositions that include two polymers, one having anionic character and one having cationic character.

An “interpenetrating polymer network,” as that term is used herein, refers to a polymer structure wherein a monomer has been polymerized in the presence of another  
 5 polymer. For example, an interpenetrating polymer network is formed by polymerizing a monomer to form the second polymer in the presence of the first polymer. An interpenetrating polymer network contains a polymer homogeneity that generally is not obtained from blending two polymers.

In one embodiment, the first polymer, the second polymer, or both the first and  
 10 the second polymer of the bimodal polymer composition have a molecular weight of at least about 1,000 daltons, for example, ranging from about 1,000 to about 1,000,000 daltons, *e.g.*, ranging from about 1,000 to about 100,000 daltons or ranging from about 2,000 to about 1,000,000 daltons. In one embodiment, the first polymer has a molecular weight ranging from about 1,000 to about 100,000 daltons and the second polymer has a  
 15 molecular weight ranging from about 2,000 to about 1,000,000 daltons. In another embodiment, the first polymer has a molecular weight ranging from about 2,000 to about 1,000,000 daltons and the second polymer has a molecular weight ranging from about 1,000 to about 100,000 daltons.

In one embodiment, the first polymer includes the carboxylate salt monomer unit  
 20 represented by Chemical Structure I:



wherein R is hydrogen or an alkyl group and X<sup>+</sup> is a salt-forming cation.



An "alkyl group," as the term is used herein, is a hydrocarbon in a molecule that is bonded to one other group in the molecule through a single covalent bond from one of its carbon atoms. Alkyl groups can be cyclic, branched or unbranched, substituted or unsubstituted, and/or saturated or unsaturated. An alkyl group can have, for example, 1  
5 to about 24 carbons atoms, 1 to about 12 carbon atoms, or about 1 to about 4 carbon atoms, *e.g.*, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl and tert-butyl.

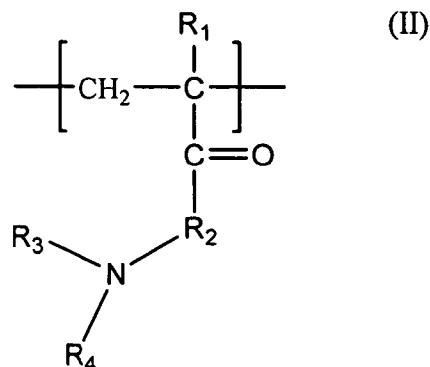
In one embodiment, the first polymer is the polymer contained in a commercially available SYNTRAN<sup>®</sup> polymer dispersion. For example, the polymer with anionic character can be the polymer contained in, for example, SYNTRAN<sup>®</sup> 1501,  
10 SYNTRAN<sup>®</sup> 1555, SYNTRAN<sup>®</sup> 1560, or in blends thereof. SYNTRAN<sup>®</sup> is a trademark of Interpolymer Corporation (Canton, MA).

SYNTRAN<sup>®</sup> 1501, SYNTRAN<sup>®</sup> 1555, and SYNTRAN<sup>®</sup> 1560 are water-based dispersions of polymers formed of acrylate monomers of the general chemical formula  $(-\text{CH}_2-\text{CH}(\text{COOR})-)_n$ . These water-based dispersions of polymers generally contain  
15 about 74 to about 75 weight percent of acrylate copolymer and about 24 to about 25 weight percent water. SYNTRAN<sup>®</sup> 1501 further contains about 1 weight percent sodium alkylpolyethoxyethanol sulfosuccinate and about 1 weight percent sodium lauryl sulfate. SYNTRAN<sup>®</sup> 1555 further contains about 1 weight percent sodium lauryl sulfate and about 1 weight percent sodium laurylpolyethoxyethanol. SYNTRAN<sup>®</sup> 1560 further  
20 contains about 1 weight percent sodium alkylpolyethoxyethanol sulfosuccinate, about 1 weight percent sodium lauryl sulfate, and about 1 weight percent sodium laurylpolyethoxyethanol.

The first polymer of the bimodal polymer composition includes, in one embodiment, at least about 10 weight percent of carboxylate salt monomer units. For  
25 example, the first polymer can include about 10 to about 20 or about 12 to about 20 weight percent of carboxylate salt monomer units.

In one embodiment, the second polymer includes the cationic monomer unit represented by Chemical Structure II:

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or a quaternized adduct thereof, wherein  $\text{R}_1$ ,  $\text{R}_3$  and  $\text{R}_4$  are, independently, hydrogen or an alkyl group and  $\text{R}_2$  is an alkyl group.

In one embodiment, the polymer with cationic character is the polymer  
 5 contained in a commercially available SYNTRAN<sup>®</sup> polymer dispersion. For example, the polymer with cationic character can be the polymer contained in, for example, SYNTRAN<sup>®</sup> FX30. SYNTRAN<sup>®</sup> FX30 is a water-based dispersion of polymer that includes diethyl amino ethyl methacrylate.

In one embodiment, the second polymer (with cationic character) includes an  
 10 ammonium derivative monomer unit. The ammonium derivative monomer unit can include, but is not limited to, dialkyl amino alkyl acrylates, dialkyl amino alkyl methacrylates, quaternized adducts of dialkyl amino alkyl acrylate, quaternized adducts of dialkyl amino alkyl methacrylate, methacrylamide and esters thereof, vinyl pyrrolidone and vinyl caprolactam. In one embodiment, the ammonium derivative  
 15 monomer unit is dimethylaminoethyl methacrylate or a quaternized adduct thereof. The second polymer can contain about 10 to about 90 weight percent of the ammonium derivative monomer unit(s). For example, the second polymer can contain about 20 to about 80, about 30 to about 70, or about 40 to about 60 weight percent ammonium derivative monomer unit(s).

In one embodiment, the second polymer includes a water insoluble monomer unit. The water insoluble monomer unit can include, but is not limited to, esters of acrylate, esters of methacrylate, ethers of acrylate, ethers of methacrylate, styrenes, and alpha-methyl styrene. In one embodiment, the water insoluble monomer unit is butyl methacrylate. The second polymer can contain about 10 to about 90 weight percent of the water insoluble monomer unit(s). For example, the second polymer can contain about 20 to about 80, about 30 to about 70, or about 40 to about 60 weight percent water insoluble monomer unit(s).

The second polymer can also include a water soluble monomer unit. For example, water soluble monomer units can include hydroxy functional acrylates, hydroxy functional methacrylates, and alkoxyated adducts thereof such as ethoxyated and/or propoxyated adducts thereof. In one particular embodiment, the second polymer includes a hydroxypropyl methacrylate monomer unit. The second polymer can contain up to about 80 weight percent of the water soluble monomer unit(s). For example, the second polymer can contain 0 to about 70, about 1 to about 50, about 5 to about 25, or about 10 to about 15 weight percent water insoluble monomer unit(s).

The second polymer can include a cross-linking or multifunctional monomer unit. For example, the second polymer can contain a multifunctional acrylate, a multifunctional methacrylate, diallyl phthalate, or any other cross-linking or multifunctional monomer units known in the art. The second polymer can contain up to about 10 weight percent of the cross-linking or multifunctional monomer unit(s). For example, the second polymer can contain 0 to about 10 such as about 1 to about 5 or about 5 to about 10 weight percent cross-linking or multifunctional monomer unit monomer unit(s).

In some embodiments, the second polymer can include a monomer unit of anionic functionality such as, but not limited to, acrylic acid, methacrylic acid and esters thereof.

In specific embodiments, the second polymer includes an ammonium derivative monomer unit, a water insoluble monomer unit, and optionally, a water soluble

monomer unit (*e.g.*, hydroxy functional acrylates, hydroxy functional methacrylates, and alkoxyated adducts thereof) and/or a cross-linking or multifunctional monomer unit.

For example, the second polymer can include about 10 to about 90 weight percent of an ammonium derivative monomer unit, about 10 to about 90 weight percent of a water

5 insoluble monomer unit, and optionally, up to about 80 weight percent of a water soluble monomer unit (*e.g.*, hydroxy functional acrylates, hydroxy functional methacrylates, and alkoxyated adducts thereof) and/or up to about 10 weight percent of a cross-linking or multifunctional monomer unit. In one particular embodiment, the second polymer includes about 55 to about 65 weight percent of dialkyl amino alkyl  
10 methacrylate, about 25 to about 35 weight percent of alkyl methacrylate, and about 5 to about 15 weight percent of hydroxy functional methacrylate. For example, the second polymer can include about 55 to about 65 weight percent of dimethylaminoethyl methacrylate, about 25 to about 35 weight percent of butyl methacrylate, and about 5 to about 15 weight percent of hydroxypropyl methacrylate.

15 In one embodiment, the first polymer is the polymer contained in SYNTRAN® 1501, SYNTRAN® 1555, SYNTRAN® 1560, or in blends thereof and the second polymer includes an ammonium derivative monomer unit, a water insoluble monomer unit, and optionally, a water soluble monomer unit and/or a cross-linking or multifunctional monomer unit, as described *supra*. The first polymer (*e.g.*, the polymer  
20 of SYNTRAN® 1501, SYNTRAN® 1555, SYNTRAN® 1560, or of blends thereof) can be present in the bimodal polymer composition in a concentration of up about 90 weight percent, for example, about 10 to about 90, about 20 to about 80, about 30 to about 70, or about 40 to about 60 weight percent. In one embodiment, the first polymer can be present in the bimodal polymer composition in a concentration of about 10 to about 30  
25 weight percent such as about 15 to about 25 weight percent. The second polymer can be present in the bimodal polymer composition in a concentration of up to about 90 weight percent, for example, about 10 to about 90, about 20 to about 80, about 30 to about 70, or about 40 to about 60 weight percent. In one embodiment, the second polymer can be

present in the bimodal polymer composition in a concentration of about 1 to about 30 weight percent such as about 5 to about 20 weight percent.

In one embodiment, the first polymer (with anionic character) includes a monomer unit with anionic functionality. The monomer unit with anionic functionality  
5 can include, but is not limited to, acidic acrylate monomer, acidic methacrylate monomer, 2-sulfoethylmethacrylate and salts thereof, 2-acrylamido-2-methyl propanesulfonate and salts thereof, crotonic acid, itaconic acid, fumaric acid, acid anhydrides, and half esters of di-carboxylate monomer. The first polymer can contain about 10 to about 90 weight percent of monomer unit(s) with anionic functionality. For  
10 example, the second polymer can contain about 20 to about 80, about 30 to about 70, or about 40 to about 60 weight percent monomer unit(s) with anionic functionality.

In one embodiment, the first polymer includes a water insoluble monomer unit. The water insoluble monomer unit can include, but is not limited to, esters of acrylate, esters of methacrylate, ethers of acrylate, ethers of methacrylate, styrenes, and  
15 alpha-methyl styrene. The first polymer can contain about 10 to about 90 weight percent of the water insoluble monomer unit(s). For example, the first polymer can contain about 20 to about 80, about 30 to about 70, or about 40 to about 60 weight percent water insoluble monomer unit(s).

The first polymer can also include a water soluble monomer unit. For example,  
20 water soluble monomers can include hydroxy functional acrylates, hydroxy functional methacrylates, and alkoxylated adducts thereof such as ethoxylated and/or propoxylated adducts thereof. The first polymer can contain up to about 80 weight percent of the water soluble monomer unit(s). For example, the first polymer can contain 0 to about 70, about 1 to about 50, about 5 to about 25, or about 10 to about 15 weight percent  
25 water insoluble monomer unit(s).

The first polymer can include a cross-linking or multifunctional monomer unit. For example, the first polymer can contain a multifunctional acrylate, a multifunctional methacrylate, diallyl phthalate, or any other cross-linking or multifunctional monomer units known in the art. The first polymer can contain up to about 10 weight percent of

the cross-linking or multifunctional monomer unit(s). For example, the first polymer can contain 0 to about 10 such as about 1 to about 5 or about 5 to about 10 weight percent cross-linking or multifunctional monomer unit monomer unit(s). In one embodiment, the first polymer also includes a chain modifier. Chain modifiers are  
5 known in the art and include, but are not limited to, alcohols and mercaptans.

In specific embodiments, the first polymer includes a monomer unit with anionic functionality, a water insoluble monomer unit, and optionally, a water soluble monomer unit (*e.g.*, hydroxy functional acrylates, hydroxy functional methacrylates, and alkoxylated adducts thereof) and/or a cross-linking or multifunctional monomer unit.  
10 For example, the first polymer can include about 10 to about 90 weight percent of a monomer unit with anionic functionality, about 10 to about 90 weight percent of a water insoluble monomer unit, and optionally, up to about 80 weight percent of a water soluble monomer unit (*e.g.*, hydroxy functional acrylates, hydroxy functional methacrylates, and alkoxylated adducts thereof) and/or up to about 10 weight percent of  
15 a cross-linking or multifunctional monomer unit.

In one embodiment, the first polymer includes a monomer unit with anionic functionality, a water insoluble monomer unit, and optionally, a water soluble monomer unit and/or a cross-linking or multifunctional monomer unit, as described *supra*, and the second polymer is the polymer contained in SYNTRAN® FX30. The first polymer can  
20 be present in the bimodal polymer composition in a concentration of up to about 90 weight percent, for example, about 10 to about 90, about 20 to about 80, about 30 to about 70, or about 40 to about 60 weight percent. In one embodiment, the first polymer can be present in the bimodal polymer composition in a concentration of about 1 to about 30 weight percent such as about 5 to about 20 weight percent. The second  
25 polymer (*e.g.*, the polymer of SYNTRAN® FX30) can be present in the bimodal polymer composition in a concentration of up about 90 weight percent, for example, about 10 to about 90, about 20 to about 80, about 30 to about 70, or about 40 to about 60 weight percent. In one embodiment, the second polymer can be present in the

bimodal polymer composition in a concentration of about 10 to about 30 weight percent such as about 15 to about 25 weight percent.

In some embodiments, substantially all or all of the carboxylate groups of a constituent polymer of the bimodal polymer composition have been neutralized, *e.g.*, as salts. Neutralization can be accomplished by techniques known in the art, for example, carboxylic acid groups of the polymer can be reacted with one or more alkaline reagents. For example, in one embodiment, the first polymer, with anionic character, contains carboxylate groups that have been neutralized, for example, by forming carboxylate salts.

10 In one embodiment, the present bimodal polymer composition includes at least about 10 weight percent of monomer units with anionic functionality. For example, the bimodal polymer composition can include at least about 20 or at least about 30 weight percent monomer units with anionic functionality. Additionally, the bimodal polymer composition can include at least about 10 weight percent of monomer units with  
15 cationic functionality. For example, the bimodal polymer composition can include at least about 20 or at least about 30 weight percent monomer units with cationic functionality.

In one specific embodiment, the bimodal polymer composition can contain less than about 40 weight percent hydroxyl-containing monomer units. For example, the  
20 bimodal polymer composition can contain less than about 30 or less than about 20 weight percent hydroxyl-containing monomer units.

In one embodiment, the glass transition temperature ( $T_g$ ) of the present bimodal polymer compositions can be indicative of the bimodal nature of the compositions. The glass transition temperature of the present bimodal polymer compositions can be less  
25 than about 40°C such as less than 30°C.

The present invention also includes methods for forming a bimodal polymer composition. The method can include the step of polymerizing monomers to form a first polymer with cationic character in the presence of a second polymer with anionic character. In one embodiment, the second polymer is represented by Chemical Structure

I, *supra*. For example, the second polymer is represented by Chemical Structure I wherein R is hydrogen.

In one embodiment, the bimodal polymer composition is formed by the free radical polymerization of the first polymer monomer components in the presence of the second polymer. For example, the bimodal polymer composition is formed by the free radical polymerization of an ammonium derivative monomer unit, a water insoluble monomer unit, and optionally, a water soluble monomer unit (*e.g.*, hydroxy functional acrylates, hydroxy functional methacrylates, and alkoxyated adducts thereof) and/or a cross-linking or multifunctional monomer unit in the presence of the second polymer (*e.g.*, the polymer contained in SYNTRAN® 1501, SYNTRAN® 1555, SYNTRAN® 1560, and blends thereof).

In one embodiment, the second polymer is dispersed in an aqueous medium. The aqueous medium can further include, for example, salts of alkylpolyethoxyethanol sulfosuccinate, salts of lauryl sulfate, and salts of laurylpolyethoxyethanol. In one embodiment, the concentration of the second polymer in the aqueous medium is about 10 to about 40 weight percent such as about 20 to about 30 weight percent or about 24 to about 25 weight percent. For example, water-dispersed polymers can be used such as, but not limited to, SYNTRAN® 1501, SYNTRAN® 1555, SYNTRAN® 1560, and blends thereof.

The reaction of this above-described monomer composition can be moved to complete, or substantially complete, conversion by conventional methods known in the art, *e.g.*, by emulsion polymerization, in water, solvent, or a combination thereof. The bimodal polymer composition thus obtained can be neutralized with an appropriate organic base or inorganic base to 0 to about 100 percent of the available carboxyl groups.

In another embodiment, a method forming a bimodal polymer composition includes the step of polymerizing monomers to form a first polymer with anionic character in the presence of a second polymer with cationic character. In one embodiment, the second polymer is represented by Chemical Structure II, *supra*, such as



diethylaminoethyl methacrylate or a quaternized adduct thereof. The bimodal polymer composition can be formed by the free radical polymerization of the first polymer monomer components in the presence of the second polymer. For example, the bimodal polymer composition is formed by the free radical polymerization of a monomer unit  
5 with anionic functionality, a water insoluble monomer unit, and optionally, a water soluble monomer unit (*e.g.*, hydroxy functional acrylates, hydroxy functional methacrylates, and alkoxylated adducts thereof) and/or a cross-linking or multifunctional monomer unit in the presence of the second polymer (*e.g.*, SYNTRAN® FX30 and the like).

10 In one embodiment, the second polymer is dispersed in an aqueous medium. The aqueous medium can further include, for example, salts of alkylpolyethoxyethanol sulfosuccinate, salts of lauryl sulfate, and salts of laurylpolyethoxyethanol. In one embodiment, the concentration of the second polymer in the aqueous medium is about 10 to about 40 weight percent such as about 20 to about 30 weight percent or about 24  
15 to about 25 weight percent. For example, a water-dispersed polymer can be used such as, but not limited to, SYNTRAN® FX30.

The reaction of this above-described monomer composition can be moved to complete, or substantially complete, conversion by conventional methods known in the art, *e.g.*, by emulsion polymerization, in water, solvent, or a combination thereof. The  
20 bimodal polymer composition thus obtained can be neutralized with an appropriate organic acid or inorganic acid to 0 to about 100 percent of the available amino groups.

General techniques associated with emulsion polymerization suitable for forming the vehicle composition of this invention are discussed in D.C. Blackley, Emulsion Polymerization (Wiley, 1975). The teachings of which are incorporated  
25 herein by reference in their entirety. Final pH can be adjusted with a suitable cosmetically acceptable base used in the cosmetic industry. If the polymer is associated with other non-cosmetic applications, other more aggressive bases may be incorporated.

The present invention also includes the bimodal polymer compositions produced by the methods described herein. In one aspect, the invention includes personal care

fixatives that include bimodal polymer compositions produced by the methods described herein.

The bimodal polymer compositions of the present invention can be used in personal care products such as personal care fixatives. For example, the bimodal polymer compositions can be used in hair fixatives such as, but not limited to, sprays, gels and mousses. In one embodiment, the invention includes a fixative composition such as a personal care fixative. The personal care fixative can include the bimodal polymer composition and a cosmetically acceptable medium. The cosmetically acceptable medium can include one or more relatively volatile solvents such as water or an alcohol. The personal care fixative can include a total volatile solvent concentration ranging from about 25 to about 95 weight percent or more, *e.g.*, about 30 to about 95, about 50 to about 95, or about 75 to about 95 weight percent total volatile solvents. In one embodiment, the cosmetically acceptable medium is principally water by weight. In some embodiments, the personal care fixative is at least about 20, 30, 40, 50, 60, 70, 80, or at least about 90 weight percent water. In addition, in some embodiments, the cosmetically acceptable medium also includes an alcohol such as ethanol or panthenol. Preferably, the concentration of volatile organic compounds (VOC) such as, for example, alcohol is less than about 55 weight percent. For example the VOC concentration can be less than about 50, 45, 40, 35, 30, 25, 20, 15, 10, or less than 5 weight percent VOC. The personal care fixative can also contain any of the personal care fixative additives known to those of skill in the art. For example, the personal care fixative further can contain at least one component selected from the group consisting of thickening agents, dispersing agents, emulsifiers, emollients, stabilizers, surfactants, fragrances, preservatives, proteins, conditioners, colorants, dyes, plasticizers, neutralizers, glossifiers and propellants.

Application of the personal care fixatives described herein to a subject (*e.g.*, to a human subject) typically produces a polymer film. The polymer film can be principally composed of the bimodal polymer composition. In one embodiment, the polymer film is easily removed using normal hygiene procedures. For example, the polymer film can

be water soluble or water dispersible. In one embodiment, the polymer film is removeable by water and soap or shampoo.

#### EXEMPLIFICATION

The invention will now be further and specifically described by the following  
5 examples which are not intended to be limiting.

##### Example 1

This example describes the production of a bimodal polymer composition.

In a 1000 ml resin flask equipped with an agitator, condensers, and addition  
ports, 500 grams SYNTRAN® 1501 (containing 25 weight percent non-volatiles) was  
10 added. The SYNTRAN® 1501 was heated to 80°C slowly with a water bath and  
keeping the flask blanketed with an inert gas. When the temperature was reached, a  
premix of 40 grams of water and 0.5 gram of ammonium persulfate was slowly added.

Immediately following, the following premix was added: 16 grams  
dimethylaminoethyl methacrylate, 8 grams butyl methacrylate, 3 grams hydroxypropyl  
15 methacrylate, 7 grams water, and 0.5 gram C12-C15 alkyl alcohol ethoxylate/10 mole.  
The reaction was allowed to exotherm and the temperature was kept between about  
80°C and about 85°C using the water bath. The temperature was held for two hours,  
then 30 grams water, 0.2 gram ammonium bisulfite (45% solution), and 0.5 gram aqua  
ammonia (28%) were added. The mixture was then held for an additional hour.

20

##### Example 2

This example describes the production of a bimodal polymer composition.

In a 1000 ml resin flask equipped with an agitator, condensers, and addition  
ports, 350 grams SYNTRAN® 1501 (containing 25 weight percent non-volatiles) and  
25 104 grams of water was added. The SYNTRAN® 1501 was heated to 60°C slowly with  
a water bath and keeping the flask blanketed with an inert gas. A slow, even agitation

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was maintained while the material was in the flask. When the temperature was reached, a premix of 40 grams of water and 0.5 gram of ammonium persulfate was slowly added.

Immediately following, the following premix was added: 25 grams dimethylaminoethyl methacrylate, 30 grams butyl acrylate, 10 grams hydroxyethyl acrylate, 15 grams water, and 1 gram C12-C15 alkyl alcohol ethoxylate/10 mole. The reaction was allowed to exotherm and the temperature was kept between about 80°C and about 85°C using the water bath. The temperature was held for two hours, then 40 grams water, 0.2 gram ammonium bisulfite (45% solution), and 0.5 gram aqua ammonia (28%) were added. The mixture was then held for an additional hour.

10

### Example 3

This example describes the preparation of mousse and gel fixatives.

### Preparation of Fixatives

15 Mousse and gel fixatives were prepared having the components listed in Tables 1 and 2. (DOW CORNING® is a trademark of Dow Corning (Midland, MI). MACKSTAT® is a trademark of The McIntyre Group Ltd. (University Park, IL). BRIJ® is a trademark of ICI Americas, Inc. (Wilmington, DE).)

20 The bimodal polymer composition used in Mousse Fixative A and the Gel Fixative was produced as described in Example 1. The bimodal polymer composition used in Mousse Fixative B was produced as described in Example 2.

**Table 1: Gel Fixative**

	<b>Component</b>	<b>Supplier</b>	<b>Concentration (weight percent)</b>	<b>Weight (grams)</b>
	<b><i>Phase A</i></b>			
	Distilled Water		72.68	218
5	Acritimer 940 (carbomer)	Rita Corp. (Woodstock, IL)	0.60	1.80
	Triethanolamine (TEA) 99%	Pride Solvents & Chemical Co. (Holtsville, NY)	0.62	1.86
	<b><i>Phase B</i></b>			
	Bimodal Polymer Composition		15	45
10	<b><i>Phase C</i></b>			
	Distilled Water		10	30
	DOW CORNING® 193 Fluid (silicon fluid)	Dow Corning (Midland, MI)	0.05	0.15
	Ritapan DL (panthenol)	Rita Corp. (Woodstock, IL)	0.10	0.30
15	Promois WG (hydrolyzed wheat protein)	Rita Corp. (Woodstock, IL)	0.05	0.15
	Promois WG-SIG (hydrolyzed wheat protein PG-Propyl Methylsilanediol)	Rita Corp. (Woodstock, IL)	0.05	0.15
20	MACKSTAT® DM-LO (DMDM Hydantoin)	The McIntyre Group Ltd. (University Park, IL)	0.40	1.20
	<b><i>Phase D</i></b>			
	BRIJ® 98 Veg (Oleth-20)	Uniqema (New Castle, DE)	0.35	1.05
	Fragrance #98444	Intarome (Norwood, NJ)	0.1	0.30
25	<b><i>Total:</i></b>		100	300

The Gel Fixative, having a composition as shown in Table 1, was prepared by mixing Phase A components. Separately, Phase C and D were mixed. Phases C and D were then warmed and then Phase D was added to Phase C. Phases C and D were then stirred until the mixture was homogeneous. The mixture of Phases C and D were then  
5 added to Phase A and stirred. Finally, Phase B was added to the mixture of Phases A, C and D and the resulting mixture was stirred until homogeneous.

**Table 2: Mousse Fixatives A and B**

	Component	Supplier	Concentration (weight percent)	Weight (grams)
	<i>Phase A</i>			
	Distilled Water		87.95	263.85
5	Ritapan DL (panthenol)	Rita Corp. (Woodstock, IL)	0.50	1.50
	DOW CORNING® 193 Fluid (silicon fluid)	Dow Corning (Midland, MI)	0.50	1.50
	Bimodal Polymer Composition		10	30
10	MACKSTAT®DM-LO (DMDM Hydantoin)	The McIntyre Group Ltd. (University Park, IL)	0.40	1.20
	Promois WG (hydrolyzed wheat protein)	Rita Corp. (Woodstock, IL)	0.10	0.30
15	Promois WG-SIG (hydrolyzed wheat protein PG-Propyl Methylsilanediol)	Rita Corp. (Woodstock, IL)	0.10	0.30
	<i>Phase B</i>			
	PEG-40 Hydrogenated Castor Oil	Lipo Chemicals, Inc. (Paterson, NJ)	0.05	0.15
20	Fragrance # 98444	Intarome (Norwood, NJ)	0.10	0.30
	Polysorbate 20 (PEG-10 Sorbitan Laurate)	Lipo Chemicals, Inc. (Paterson, NJ)	0.30	0.90
	<b>Total:</b>		100	300

25 Mousse Fixatives A and B, having compositions as shown in Table 2, were prepared by adding together Phase A components in the listed order followed by stirring until Phase A was homogeneous. Phase B was then prepared by mixing the listed

components. Phase B was added to Phase A and the mixture was stirred until homogeneous.

### **Evaluation of Fixative Compositions**

Several 24 cm tresses of European Brown hair (from same lot of hair) were  
5 prepared. Each tress weighed about 6.5 grams. Each tress was washed thoroughly with a strong detergent to remove any residual materials and excess water was removed.

#### **Mousse Application**

About 0.5 grams of mousse fixative was applied to each of a set of tresses and was gently spread through the hair. The tips of the hair were then rolled about a 3/4  
10 inch to 1 inch curling rod. The tresses were clamped to the curling rods and dried for about five days in air at room temperature.

#### **Gel Application**

About 0.8 grams of the gel fixative was applied to each of a set of tresses and  
15 was gently spread through the tresses. Each tress was then combed through tress once with fine end of a comb to distribute the gel fixative composition. The tips of the hair were then rolled about a 3/4 inch to 1 inch curling rod. The tresses were clamped to the curling rods and dried for about 5 days in air at room temperature.

20 The dry hair was removed from the curling rods and hung on calibrated boards. The length of the curl was measured. The curled hair was placed in a humidity chamber and position of bottom of curl was noted at prescribed time intervals. The humidity chamber had an average temperature of 82.7°F and an average humidity of 96.7 percent relative humidity. Table 3 shows the percent curl retention for the Gel Fixative, Mousse  
25 Fixatives A and B, and 3 comparative fixatives (CARBOPOL® Polymer Gel, PVP K90 Mousse, and PVP K30 Mousse). The comparative fixatives were prepared by substituting a CARBOPOL® polymer, polyvinyl pyrrolidone (PVP) K90 and PVP K30,



respectively, for the bimodal polymer composition in the gel and mousse formulations of Tables 1 and 2. CARBOPOL® is a trademark of Noveon IP Holdings Corp. (Cleveland, OH). The PVP K90 and PVP K30 were obtained from ISP Technologies, Inc. (Wayne, NJ).

5

**Table 3: Hair Curl Retention Using Various Fixatives**

		Gel Fixative	CARBOPOL <sup>®</sup> Polymer Gel	PVP K90 Mousse	Mouse Fixative A	PVP K30 Mousse	Mouse Fixative B
10	Initial Curl Length (cm)	4.4	4.5	4.0	4.0	3.7	4.5
	Final Curl Length (cm)	6.5	15.3	12.1	4.7	16.0	6.5
15	Time (hours)	Curl Retention Percentage:					
	1	96.9	97.4	96.0	100	81.3	92.8
	2	94.4	66.7	96.5	100	64	92.3
	3	89.8	48.7	73.5	96.5	46.8	89.7
	4	89.8	44.6	65	96.5	41.9	89.7
	5	89.3	44.6	59.5	96.5	39.4	89.7

20

**Example 4**

This example describes three hair fixative compositions.

**Pump Composition A – (Crisp Character) (5% non-volatiles)**

	bimodal polymer composition	20 grams (g)
25	water	24.6 g

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amino methyl propanol (AMP)	0.4 g
ethyl alcohol, denatured (SDA-40)	55 g

The water, SDA-40 and AMP are mixed and the bimodal polymer composition is slowly added with good agitation until dispersed.

5 Pump Composition B – (Flexible Hold) (5% non-volatiles)

	bimodal polymer composition	20 grams (g)
	water	23.3 g
	amino methyl propanol (AMP)	0.5 g
	Crovol PK-70	
10	(Croda, Inc., Parsippany, NJ)	0.4 g
	DOW CORNING® 190 Fluid	
	(Dow Corning Midland, MI)	0.4 g
	1,3-butylene glycol	0.4 g
	ethyl alcohol, denatured (SDA-40)	55.0 g

- 15 All ingredients except for the bimodal polymer composition are mixed with good agitation. The bimodal polymer composition is then added to the mixture with continued agitation.

Pump Composition C – (Low Static) (5% non-volatiles)

	bimodal polymer composition	14.4 grams (g)
20	water	21.9 g
	amino methyl propanol (AMP)	0.5 g
	Crovol PK-70	
	(Croda, Inc., Parsippany, NJ)	0.8 g
	DOW CORNING® 190 Fluid	
25	(Dow Corning Midland, MI)	1.2 g

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panthenol	0.8 g
ethyl alcohol, denatured (SDA-40)	55 g
Statran 1705	
(Interpolymer Corp, Canton, MA)	1.2 g

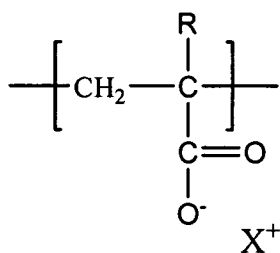
5           All of the ingredients are mixed with good agitation except the bimodal polymer composition and Statran 1705. The Statran 1705 is slowly added and allowed to mix. After the Statran 1705 is dispersed, the bimodal polymer composition is slowly added and agitated until dispersed.

10           While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

## CLAIMS

We claim:

1. A bimodal polymer composition, comprising a first polymer with anionic character and a second polymer with cationic character, wherein the polymers form an interpenetrating polymer network.
2. The bimodal polymer composition of Claim 1 wherein the first polymer has a molecular weight ranging from about 1,000 to about 100,000 daltons.
3. The bimodal polymer composition of Claim 1 wherein the second polymer has a molecular weight ranging from about 2,000 to about 1,000,000 daltons.
4. The bimodal polymer composition of Claim 1 wherein the first polymer includes the following carboxylate salt monomer unit:



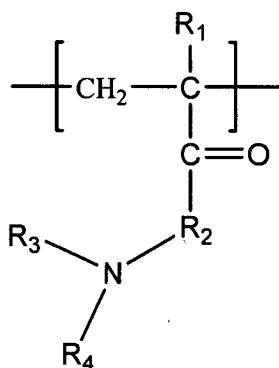
wherein R is hydrogen or an alkyl group and X<sup>+</sup> is a salt-forming cation.

5. The bimodal polymer composition of Claim 4 wherein the first polymer contains at least about 10 weight percent of carboxylate salt monomer units.

6. The bimodal polymer composition of Claim 5 wherein the first polymer contains about 10 to about 20 weight percent carboxylate salt monomer units.
7. The bimodal polymer composition of Claim 6 wherein the first polymer contains about 12 to about 20 weight percent carboxylate salt monomer units.
- 5 8. The bimodal polymer composition of Claim 1 wherein the second polymer includes an ammonium derivative monomer unit.
9. The bimodal polymer composition of Claim 8 wherein the second polymer includes about 10 to about 90 weight percent ammonium derivative monomer unit.
- 10 10. The bimodal polymer composition of Claim 8 wherein the ammonium derivative monomer unit is selected from the group consisting of: dialkyl amino alkyl acrylates, dialkyl amino alkyl methacrylates, quaternized adducts of dialkyl amino alkyl acrylate, quaternized adducts of dialkyl amino alkyl methacrylate, methacrylamide and esters thereof, vinyl pyrrolidone, and vinyl caprolactam.
- 15 11. The bimodal polymer composition of Claim 10 wherein the ammonium derivative monomer unit is dimethylaminoethyl methacrylate or a quaternized adduct thereof.
12. The bimodal polymer composition of Claim 1 wherein the second polymer  
20 includes a water insoluble monomer unit.
13. The bimodal polymer composition of Claim 12 wherein the second polymer includes about 10 to about 90 weight percent water insoluble monomer unit.

14. The bimodal polymer composition of Claim 12 wherein the water insoluble monomer unit is selected from the group consisting of: esters of acrylate, esters of methacrylate, ethers of acrylate, ethers of methacrylate, styrene, and alpha-methyl styrene.
- 5 15. The bimodal polymer composition of Claim 14 wherein the water insoluble monomer unit is butyl methacrylate.
16. The bimodal polymer composition of Claim 1 wherein the second polymer includes a water soluble monomer unit selected from the group consisting of: hydroxy functional acrylates, hydroxy functional methacrylates, and  
10 alkoxylated adducts thereof.
17. The bimodal polymer composition of Claim 16 wherein the second polymer includes up to about 80 weight percent of the water soluble monomer unit.
18. The bimodal polymer composition of Claim 16 wherein the water soluble  
15 monomer unit is hydroxypropyl methacrylate.
19. The bimodal polymer composition of Claim 1 wherein the second polymer includes a cross-linking or multifunctional monomer unit.
20. The bimodal polymer composition of Claim 19 wherein the second polymer  
20 includes up to about 10 weight percent of the cross-linking or multifunctional monomer unit.
21. The bimodal polymer composition of Claim 19 wherein the cross-linking or multifunctional monomer unit is selected from the group consisting of multifunctional acrylates, multifunctional methacrylates and diallyl phthalate.

22. The bimodal polymer composition of Claim 1 wherein the second polymer includes a monomer unit of anionic functionality.
23. The bimodal polymer composition of Claim 22 wherein the monomer unit of anionic functionality is selected from the group consisting of: acrylic acid, methacrylic acid and esters thereof.
24. The bimodal polymer composition of Claim 1 wherein the second polymer includes the following cationic monomer unit:



- or a quaternized adduct thereof,  
 wherein  $\text{R}_1$ ,  $\text{R}_3$  and  $\text{R}_4$  are, independently, hydrogen or an alkyl group and  $\text{R}_2$  is an alkyl group.
25. The bimodal polymer composition of Claim 24 wherein the cationic monomer unit includes diethylaminoethyl methacrylate or a quaternized adduct thereof.

26. The bimodal polymer composition of Claim 1 wherein the second polymer contains at least about 10 weight percent cationic monomer units.
27. The bimodal polymer composition of Claim 26 wherein the second polymer contains about 10 to about 20 weight percent cationic monomer units.
- 5 28. The bimodal polymer composition of Claim 27 wherein the second polymer contains about 12 to about 20 weight percent of cationic monomer units.
29. The bimodal polymer composition of Claim 1 wherein the second polymer has a molecular weight ranging from about 1,000 to about 100,000 daltons.
30. The bimodal polymer composition of Claim 1 wherein the first polymer has a  
10 molecular weight ranging from about 2,000 to about 1,000,000 daltons.
31. The bimodal polymer composition of Claim 1 wherein the first polymer includes a monomer unit with anionic functionality selected from the group consisting of acidic acrylate monomer; acidic methacrylate monomer;  
2-sulfoethylmethacrylate and salts thereof; 2-acrylamido-2-methyl  
15 propanesulfonate and salts thereof; crotonic acid; itaconic acid, fumaric acid; acid anhydrides; and half esters of di-carboxylate monomer.
32. The bimodal polymer composition of Claim 1 wherein the first polymer includes about 10 to about 90 weight percent monomer unit with anionic functionality.
- 20 33. The bimodal polymer composition of Claim 1 wherein the first polymer includes a water insoluble monomer unit.



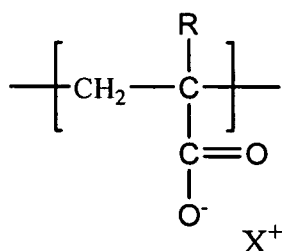
34. The bimodal polymer composition of Claim 33 wherein the first polymer includes about 10 to about 90 weight percent water insoluble monomer unit.
35. The bimodal polymer composition of Claim 33 wherein the water insoluble monomer unit is selected from the group consisting of: esters of acrylate, esters of methacrylate, ethers of acrylate, ethers of methacrylate, styrene, and alpha-methyl styrene.
36. The bimodal polymer composition of Claim 1 wherein the first polymer includes a water soluble monomer unit selected from the group consisting of: hydroxy functional acrylates, hydroxy functional methacrylates, and alkoxylated adducts thereof.
37. The bimodal polymer composition of Claim 36 wherein the first polymer includes to up about 80 weight percent of the water soluble monomer unit.
38. The bimodal polymer composition of Claim 1 wherein the first polymer includes a cross-linking or multifunctional monomer unit.
39. The bimodal polymer composition of Claim 38 wherein the first polymer includes up to about 10 weight percent cross-linking or multifunctional monomer unit.
40. The bimodal polymer composition of Claim 38 wherein the cross-linking or multifunctional monomer unit is selected from the group consisting of multifunctional acrylates, multifunctional methacrylates and diallyl phthalate.
41. The bimodal polymer composition of Claim 1 wherein the first polymer includes a chain modifier.

42. The bimodal polymer composition of Claim 41 wherein the chain modifier is an alcohol or a mercaptan.
43. The bimodal polymer composition of Claim 1 wherein the first polymer is present in a concentration of about 10 to about 90 weight percent.
- 5 44. The bimodal polymer composition of Claim 1 wherein the second polymer is present in a concentration of about 10 to about 90 weight percent.
45. The bimodal polymer composition of Claim 1 wherein the glass transition temperature ( $T_g$ ) of the composition is less than about 40°C.
- 10 46. The bimodal polymer composition of Claim 45 wherein the glass transition temperature of the composition is less than about 30°C.
47. The bimodal polymer composition of Claim 1 containing less than about 40 weight percent of a hydroxyl-containing monomer.
48. The bimodal polymer composition of Claim 47 containing less than about 30  
15 weight percent of a hydroxyl-containing monomer.
49. The bimodal polymer composition of Claim 1 containing at least about 10 weight percent of monomer units with anionic functionality.
50. The bimodal polymer composition of Claim 49 containing at least about 20 weight percent of monomer units with anionic functionality.
- 20 51. The bimodal polymer composition of Claim 1 containing at least about 10 weight percent of monomer units with cationic functionality.

52. The bimodal polymer composition of Claim 51 containing at least about 20 weight percent of monomer units with cationic functionality.
53. A personal care fixative containing the bimodal polymer composition of Claim 1.
54. The personal care fixative of Claim 53 further including one or more volatile solvents.
55. The personal care fixative of Claim 54 having a total volatile solvent concentration ranging from about 30 to about 95 weight percent.
56. The personal care fixative of Claim 53 further including a neutralizing agent.
57. The personal care fixative of Claim 53 further including an alcohol.
58. The personal care fixative of Claim 53 further including at least one component selected from the group consisting of thickening agents, dispersing agents, emulsifiers, emollients, stabilizers, surfactants, fragrances, preservatives, proteins, conditioners, colorants, dyes, plasticizers, neutralizers, glossifiers and propellants.
59. A method for fixing a keratin-type structure, comprising the step of applying the personal care fixative of Claim 53 to the keratin-type structure.
60. The method of Claim 59 wherein the keratin-type structure includes hair.
61. The method of Claim 60 wherein the keratin-type structure includes skin.

62. A method for forming a bimodal polymer composition, comprising the step of polymerizing monomers to form a first polymer with cationic character in the presence of a second polymer with anionic character.

63. The method of Claim 62 wherein the second polymer includes the following  
5 carboxylate salt monomer unit:



wherein R is hydrogen or an alkyl group and  $\text{X}^+$  is a salt-forming cation.

64. The method of Claim 63 wherein R is hydrogen.

10 65. The method of Claim 63 wherein the second polymer is dispersed in an aqueous medium.

66. The method of Claim 65 wherein the aqueous medium includes at least one compound selected from the group consisting of: salts of alkylpolyethoxyethanol sulfosuccinate, salts of lauryl sulfate and salts of laurylpolyethoxyethanol.

15 67. The method of Claim 65 wherein the concentration of the second polymer in the aqueous medium is about 10 to about 40 weight percent.

68. The method of Claim 67 wherein the concentration of the second polymer in the aqueous medium is about 20 to about 30 weight percent.

69. The method of Claim 68 wherein the concentration of the second polymer in the aqueous medium is about 24 to about 25 weight percent.

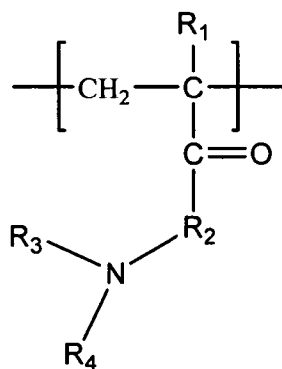
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70. The method of Claim 62 wherein emulsion polymerization is used to polymerize monomers to form the first polymer in the presence of the second polymer.

71. A method for forming a bimodal polymer composition, comprising the step of polymerizing monomers to form a first polymer with anionic character in the presence of a second polymer with cationic character.

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72. The method of Claim 71 wherein the second polymer includes the following cationic monomer unit:



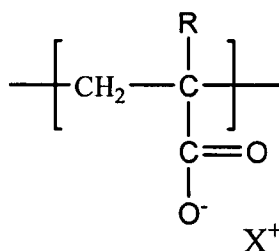
or a quaternized adduct thereof,

15

wherein  $\text{R}_1$ ,  $\text{R}_3$  and  $\text{R}_4$  are, independently, hydrogen or an alkyl group and  $\text{R}_2$  is an alkyl group.

73. The method of Claim 72 wherein the cationic monomer unit includes diethyl amino ethyl methacrylate or a quaternized adduct thereof.
74. The method of Claim 71 wherein the second polymer is dispersed in an aqueous medium.
- 5 75. The method of Claim 74 wherein the aqueous medium includes at least one compound selected from the group consisting of: salts of alkylpolyethoxyethanol sulfosuccinate, salts of lauryl sulfate and salts of laurylpolyethoxyethanol.
76. The method of Claim 74 wherein the concentration of the second polymer in the aqueous medium is about 10 to about 40 weight percent.
- 10 77. The method of Claim 76 wherein the concentration of the second polymer in the aqueous medium is about 20 to about 30 weight percent.
78. The method of Claim 77 wherein the concentration of the second polymer in the aqueous medium is about 24 to about 25 weight percent.
- 15 79. The method of Claim 71 wherein emulsion polymerization is used to polymerize monomers to form the first polymer in the presence of the second polymer.
80. A method for forming a bimodal polymer composition, comprising the step of polymerizing monomers to form a first polymer with cationic character in the presence of a second polymer with anionic character wherein the first polymer is  
20 formed from a monomer composition including about 35 to about 45 weight percent ammonium derivative monomer, about 15 to about 30 weight percent water insoluble monomer, and about 5 to about 15 weight percent water soluble monomer.

81. The method of Claim 80 wherein the second polymer includes the following carboxylate salt monomer unit:



- 5        wherein R is hydrogen or an alkyl group and X<sup>+</sup> is a salt-forming cation.
82. The method of Claim 81 wherein the second polymer is dispersed in an aqueous medium.
83. The method of Claim 82 wherein the aqueous medium includes at least one compound selected from the group consisting of: salts of alkylpolyethoxyethanol  
10        sulfosuccinate, salts of lauryl sulfate and salts of laurylpolyethoxyethanol.
84. The method of Claim 82 wherein the concentration of the second polymer in the aqueous medium is about 24 to about 25 weight percent.
85. The method of Claim 80 wherein the weight ratio of the first polymer to the  
15        second polymer is about 0.1 to about 2.
86. The method of Claim 85 wherein the weight ratio of the first polymer to the second polymer is about 0.5 to about 1.5.

- 87. The method of Claim 85 wherein the weight ratio of the first polymer to the second polymer is about 0.1 to about 0.3.
- 88. The method of Claim 87 wherein the weight ratio of the first polymer to the second polymer is about 0.15 to about 0.25.
- 5 89. A bimodal polymer composition formed by the method of Claim 80.



## ABSTRACT OF THE DISCLOSURE

The present invention is directed to bimodal polymer compositions and personal care fixatives containing bimodal polymer compositions. The present invention includes a bimodal polymer composition having a first polymer with anionic character  
5 and a second polymer with cationic character and wherein the polymers form an interpenetrating polymer network. In one embodiment, the present invention also includes personal care fixatives (*e.g.*, health care, hygiene or cosmetic compositions) containing the bimodal polymer composition. The present invention also includes methods for forming bimodal polymer compositions.